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CORROSION OF STEEL
IN A BLACK MANGROVE ENVIRONMENT

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Under the In-House Independent Laboratory Research (ILIR) Program, the US Army Tropic Test Center conducted an investigation to determine the cause of high steel corrosion rates observed at a black mangrove forest site during previous methodology investigations. The mechanism for the steel corrosion at the black mangrove forest site has been identified to be as follows: rain water falling through the mangrove canopy picks up salts and tannins from the black mangroves. The salts attack steel, forming water-soluble ferric ions. The tannins react

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with the ferric ions forming a hygroscopic, water-soluble complex; when tannins are not present, the ferric ions are precipitated as water-insoluble oxides. These oxides form a protective layer over the base metal. Thus, corrosion rates in the presence of tannins are high for two reasons: (1) the hygroscopic nature of the iron-tannin complex keeps the material surface wet and (2) the protective layer of oxide is not formed.

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CORROSION OF STEEL IN A BLACK MANGROVE ENVIRONMENT

I. BACKGROUND

During a US Army Tropic Test Center (USATTC) methodology investigation of materials degradation at 16 selected exposure sites in the humid tropics of Panama, unexpectedly high corrosion rates were noted for steel samples exposed in an experimental, mangrove forest site.[1] This site, located in Coco Solo, on the Atlantic side of the Isthmus of Panama, was found to be more severe than other types of sites throughout the Isthmus in terms of steel corrosion. Humidity and atmospheric salt levels at the mangrove forest site were comparable to levels at the other sites. Unique factors contributing to this unusually severe steel degradation at the mangrove site were not determined in the referenced investigation.

To determine if the severe corrosion of steel at the mangrove forest site was a general property of all mangrove forests, a second methodology investigation was conducted.[2] Steel samples were exposed at seven mangrove forest sites throughout the Panama area. The Fort Sherman Marine Breakwater Exposure site was used as a control site. Results of this investigation showed a high degree of correlation between tensile strength loss and conductivity of runoff water collected from mangrove trees. The primary cause of high conductivity in runoff water was the presence of water-soluble salts. These salts were exuded from the leaves of some mangrove species and also were deposited by coastal winds. They were washed from the mangrove trees by rainfalls. Table 1 relates conductivity to chloride content at the seven mangrove forest sites.

The second investigation revealed that, during both dry and wet seasons, degradation rates at the original mangrove forest site (Coco Solo Site A) were more severe than those at other mangrove forest sites. Additionally, the degradation rates were found to be higher than those measured at the control site (Fort Sherman Marine Breakwater Exposure Site) during the wet season, but not during the dry season. Coco Solo Site A was the only test location containing _Avicennia nitida_ (black mangrove) as the predominant tree species. _Laguncularia racemosa_ (white mangrove) also was found at this site. Salt concentration in leaves at this site was 3 to 16 times greater than that found at the other forest sites.

[1] AD No. A005017, Determination of Optimum Tropic Storage and Exposure Sites Report II: Empirical Data, US Army Tropic Test Center, Fort Clayton, APO Miami 34004, J. F. Sprouse, M. D. Neptune, and J. C. Bryan, TECOM Project No. 9-CO-009-000-006, USATTC Report No. 7403001, March 1974.

[2] AD No. A054-969, Methodology Investigation: Steel Corrosion in Tropic Mangrove Forest, US Army Tropic Test Center, Fort Clayton, APO Miami 34004, M. A. Johnson and G. F. Downs III, TECOM Project No. 7-CO-RD5-TT1-016, USATTC Report No. 7511002, November 1975.

TABLE 1. AVERAGE ELECTROLYTE STRENGTH OF RUN-OFF WATER DURING WET SEASON

SITES	CONDUCTIVITY (mho/cm)	CHLORIDE (ppm)
Pacific Side		
Kobbe Mangrove	7.72×10^{-5}	18.0
Rodman Mangrove	1.00×10^{-4}	26.2
Atlantic Side		
Sherman Mangrove A	8.91×10^{-5}	29.1
Sherman Mangrove B	1.00×10^{-4}	17.2
Coco Solo Mangrove B	1.29×10^{-4}	49.5
Galeta Point Mangrove	1.02×10^{-4}	34.6
Coco Solo Mangrove A	3.80×10^{-4}	221.2

NOTE: Conductivity and chloride content data are averages for samples collected during the wet season--23 September 1973 to 9 January 1974.

The fact that corrosion rates at the Coco Solo Site A were much higher than at the Fort Sherman Marine Breakwater Exposure site, where atmospheric salt levels were much higher, initiated interest in the corrosion process that occurred in the Coco Solo Site A.

II. OBJECTIVE

Investigate the cause of high steel corrosion rates observed at a black mangrove forest site during previous methodology investigations.

III. METHODS

a. Materials: All steel used in this project was 0.025 centimeter (cm) thick shimstock steel (AISI 1006 carbon steel).

b. Comparison Data: The results obtained during another USATTC methodology study,[3] where steel was exposed at the Fort Sherman Coastal Exposure site, were used as references for comparison purposes.

c. Natural Exposure: Six (15.2 by 10.2 cm) steel samples were weighed before being placed on exposure at Coco Solo Site A (figure 1). The samples

[3]Draft, Methodology Investigation: Tropic vs CONUS. Correlation Tests, US Army Tropic Test Center, Fort Clayton, APO Miami 34004, F. Chen and W. A. Dement, TECOM Project No. 7-CO-RD8-TT1-001, USATTC Report No. 820703, unpublished.

were exposed horizontally, on racks about 60 centimeters above ground level. After 4 days of exposure, the samples were retrieved for laboratory analysis. The retrieved steel samples were inspected visually and the physical nature and color of the corrosion products were determined. The extent and pattern of the sample surface corrosion also were determined. Corrosion weight losses (CWL) of the exposed steel samples were determined using ASTM standard G-1.[4] The samples were weighed again after corrosion products had been removed chemically. Detailed observations of the exposed surfaces were made with a scanning electron microscope (SEM). A small area (about 1 by 1 cm) was cut from the test sample. This piece was mounted on an aluminum SEM stub with colloidal graphite adhesive and sputter-coated with gold to improve its conductive properties.

d. Rainwater Analysis: Rainwater, together with runoff water, was collected by emplacing sampling bottles, with funnels inserted into the tops, under the mangrove canopy adjacent to the exposure rack. Analyses were performed on the water samples for chlorides and phenolic oxidizing compounds using colorimetric method. The chloride analysis was based on its color reaction with ferric nitrate and mercuric thiocyanate and was accomplished using a Technicon Autoanalysis System. The test for phenols and tannins was based on the color development after their reaction with Folin's Reagent. Absorption readings at 550 nanometers were made and evaluated based on absorption readings from standard solutions of tannic acid.

e. Laboratory Exposure: To investigate the corrosion of the mangrove forest sites in the laboratory, steel samples were exposed in three different modes: immersion, drip, and in a humidity chamber. The immersion test was used to differentiate the roles of phenolic acids and salt solutions in the oxidation process. The drip test was performed to simulate exposure in mangrove forests. The humidity chamber test investigated the role of hygroscopic surface contaminants in the corrosion process. Tannic acid was used as a simulant for the laboratory test because mangroves are known to produce high levels of tannins.

(1) Immersion tests: Three different aqueous solutions were used for these tests, 20 parts-per-million (ppm) sodium chloride, 20 ppm tannic acid, and 20 ppm of both sodium chloride and tannic acid. Three 250 ml Erlenmeyer flasks were used for each solution. Each flask contained 150 ml of solution. One 15.2 x 2.5 centimeter steel strip was placed in each flask. The immersed area was about 6.5 cm^2. The strips were left immersed for four days. During this period, the immersed samples and solutions were inspected visually on a daily basis. After four days, the strips were removed and examined visually and with an SEM. Solutions were filtered and

[4]American Society for Testing Materials, Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, G-1, ASTM, Philadelphia, PA, 1978.

the filtrate examined by atomic absorption spectrometry (AAS) for soluble iron products. The insoluble corrosion products collected on the filter paper were redissolved in 100 ml of 6N hydrochloric acid and analyzed for iron by AAS.

(2) Drip tests: Three 7.6 cm steel square samples were used for this test with each drip solution. The drip solutions were sodium chloride, 300 ppm; tannic acid, 20 ppm; and sodium chloride and tannic acid, each 20 ppm. Each steel square was mounted horizontally in a 500 ml beaker and a solution was dripped onto the surface from a burette placed 30 cm above it at a rate of 20 drops per minute for 2 hours a day. The steel samples were not in contact with resulting runoff water. Each drip test lasted four days. After each test, CWL was determined for each sample using ASTM standard G-1. Each sample was visually inspected and examined further with an SEM.

(3) Humidity chamber tests: Three 5.1 cm square steel samples were placed inside each of four glass chambers with ground glass tops. A layer of water was placed in the bottom of each chamber to maintain the relative humidity at near saturation level. The temperature was about 30°C. Three sets of samples were sprinkled with surface contaminants (i.e., sodium chloride, tannic acid, and sodium chloride plus tannic acid, respectively). The fourth set was placed in its chamber with no surface contaminant. About 25 percent of the samples surfaces were covered with contaminant material.

IV. RESULTS

a. The samples exposed at the Coco Solo Mangrove Site exhibited considerable corrosion. The CWL averaged 12 percent after four days exposure. In contrast, the CWL at the Fort Sherman Coastal Site averaged 1.5 percent after seven days exposure. Visual inspection of the exposed samples revealed that only portions of top and bottom surfaces were corroded heavily. The corrosion pattern was associated with marks left on samples by runoff water. The rust was flaky and its color ranged from dark brown-black to light orange. SEM analysis showed varying degrees of attack. The heaviest corrosion was along lamination grooves where pits had been formed. Other surface portions were found to be less attacked (figures 2 and 3). In contrast, the samples exposed at the Coastal site exhibited a fairly uniform layer of orange, granular corrosion products over their surfaces.

b. Chemical analysis of runoff water collected from the exposed samples indicated the presence of dissolved salts (about 300 ppm of chloride) and unidentified polyphenolic plant products (about 5 ppm).

c. SEM examination of black mangrove leaves from Coco Solo Site A showed them to be covered by small salt crystals. Occasionally, large clusters were observed (figure 4). Crystals were formed by evaporation of a concentrated salt solution which is secreted from the lower surfaces of black mangrove leaves.

d. In the immersion test, the tannic acid solution attacked the steel sample immediately at its bottom and side edges and in the area where the sample cut the solution's surface. The area of attack was characterized by a dark-colored tarnish. The solution turned blue and remained that color throughout the 4-day immersion test. Visual inspection of the immersed portion revealed that some sections exhibited dark streaks. SEM examination of these sections indicated some areas much more heavily corroded than others. A well defined borderline between the two differently corroded areas could be observed (figure 5). The chloride solution reacted differently, attacking the entire surface of the steel sample. The solution turned yellow and insoluble corrosion products accumulated on the bottom of the flask. The solution pH had increased from 6.5 to 7.2 after one day. SEM examination after exposure revealed the formation of a large number of small pinholes and that corrosion had taken over its entire surface. The observed surface corrosion was more extensive but less localized than that observed for the tannin solution attack (figure 6). The effect of the solution (containing both tannic acid and sodium chloride, 20 ppm each) was most pronounced where the liquid level crossed the steel sample surfaces (vapor/liquid interface). The steel sample exhibited the dark blue tarnish almost immediately, and the solution started to turn blue. However, after a few hours, the solution started to change color, becoming yellowish. Insoluble corrosion products accumulated at the bottom of the flask. The color of the solution after four days was dull green. Analyses of the soluble and insoluble iron corrosion products by AAS provided different results for the different solutions. The sodium chloride solution had the highest level of insoluble products (87 ppm) and undetectable levels of soluble products. The tannic acid solution was at the opposite extreme with very low levels of insolubles (6 ppm) and highest levels of solubles (31 ppm). The solution with both sodium chloride and tannic acid was similar to the tannic acid solution having slightly more insolubles (14 ppm) and less solubles (15 ppm).

e. The CWL results for the drip test averaged 4.4 percent for samples exposed to the sodium chloride solution, 1.9 percent for those exposed to tannic acid solution, and 10 percent for those exposed to tannic acid plus sodium chloride solution. The corrosion occurred over the entire surfaces of the samples which had been wetted by the solutions. SEM examination of the samples exposed to the sodium chloride and tannic acid solution showed it to be corroded over the entire surface, and that the corrosion was similar but not as localized as in the case of steel samples exposed in the mangrove environment. Figure 7 shows the initial destruction of the steel surface by pinholes, delamination of the surface, and formation of corrosion products.

f. The clean samples that were exposed for 4 days in the humidity chamber were dry and were not rusted. However, in less than an hour, water drops could be observed on sample surfaces which had been sprinkled with sodium chloride, tannic acid, and sodium chloride plus tannic acid. These test samples were found to be covered extensively by water and heavily rusted after four days in the humidity chamber.

V. DISCUSSION

The experimental test results indicate that the phenolic acids (tannins) in the runoff water play a very important role in the observed heavy corrosion of steel at the mangrove forest site. The blue-colored tarnish and the blue solution are due to the formation of a water-soluble complex between ferric ions and the phenolic acids (formation of a blue-black complex is a test commonly used to identify phenolic-type compounds with ferric ions). The presence of ferric ions in solution is corraborated by AAS and the fact that little or no rust was observed at the bottom of the flask with steel samples immersed in tannic acid solution. The importance of tannins is also evidenced by the much higher CWL obtained in the drip test when tannic acid was added to the sodium chloride solution. Other evidences include the heavy surface dissolution when the samples were immersed in the tannin solution.

The high corrosion rate for steel samples exposed at Coco Solo Site A can be explained by the following mechanisms: Oxygen-saturated rainwater falling through the forest canopy picks up sodium chlorides and phenolic acids from black mangrove leaves. Salts and phenolic acids in the rainwater attack steel by forming soluble ferric ions. These ferric ions are precipitated from the solution by oxygen and hydroxides to form oxides. However, phenolic acids will keep the ferric ions in solution by forming a blue-black, water-soluble complex which frees chlorides and oxygen for continued attack. These water-soluble complexes are washed away when there is enough condensed moisture or rain on the sample. This removal prevents the buildup of insoluble corrosion products which normally protect the underlying base metal. Because sodium chloride, ferric chloride, phenolic acids, and the iron-phenolic complex are hygroscopic substances, they retain enough water at the material surface and promote the oxidation process.

VI. CONCLUSION

High corrosion rates for steel observed at a mangrove forest site in the tropics were the result of high levels of sodium chloride and natural plant products (phenolic acids) which were washed from the leaves of the black mangrove trees onto the exposed samples. Because many woody plants are known to produce and "leak" phenolic compounds, this phenomenon may be an important, yet unrecognized, factor contributing to corrosion of steel in forest environments.

Photographic Documentation

Figure 1. Coco Solo Site A.

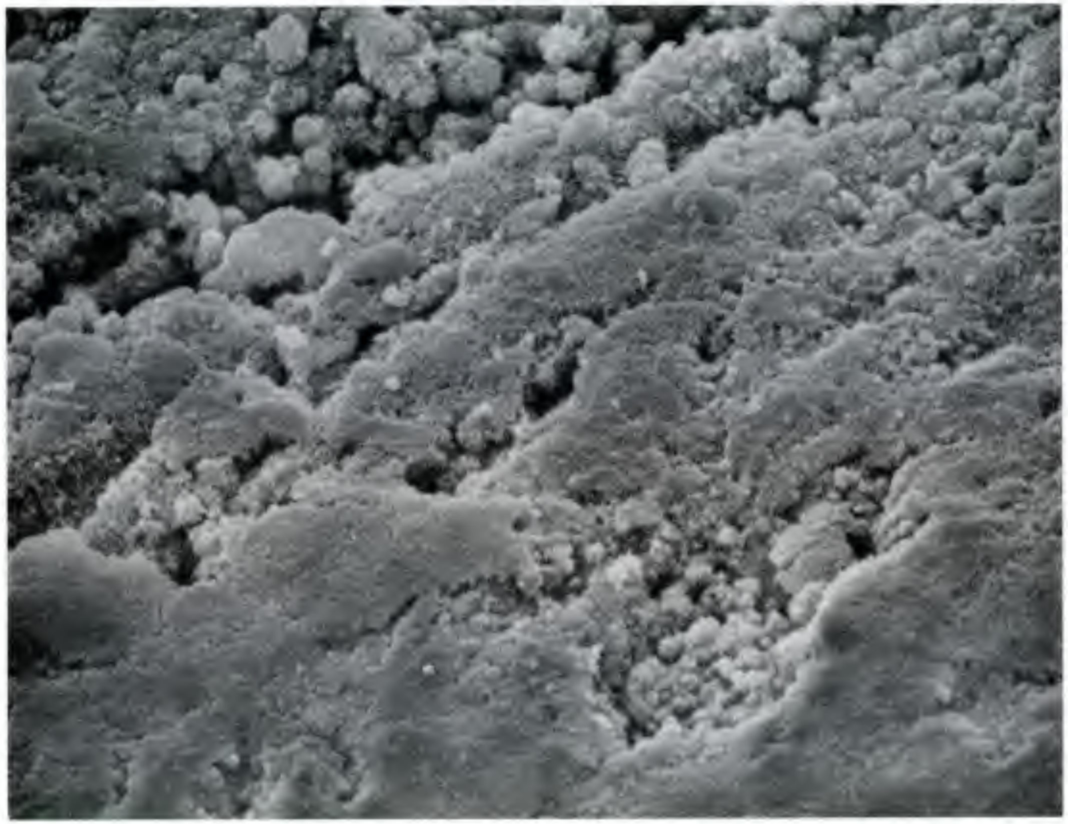

Figure 2. Top Layer of Steel Surface Had Reacted. Heaviest Reaction Took Place Along Lamination Grooves. Mangrove Forest Exposure, 1000x.

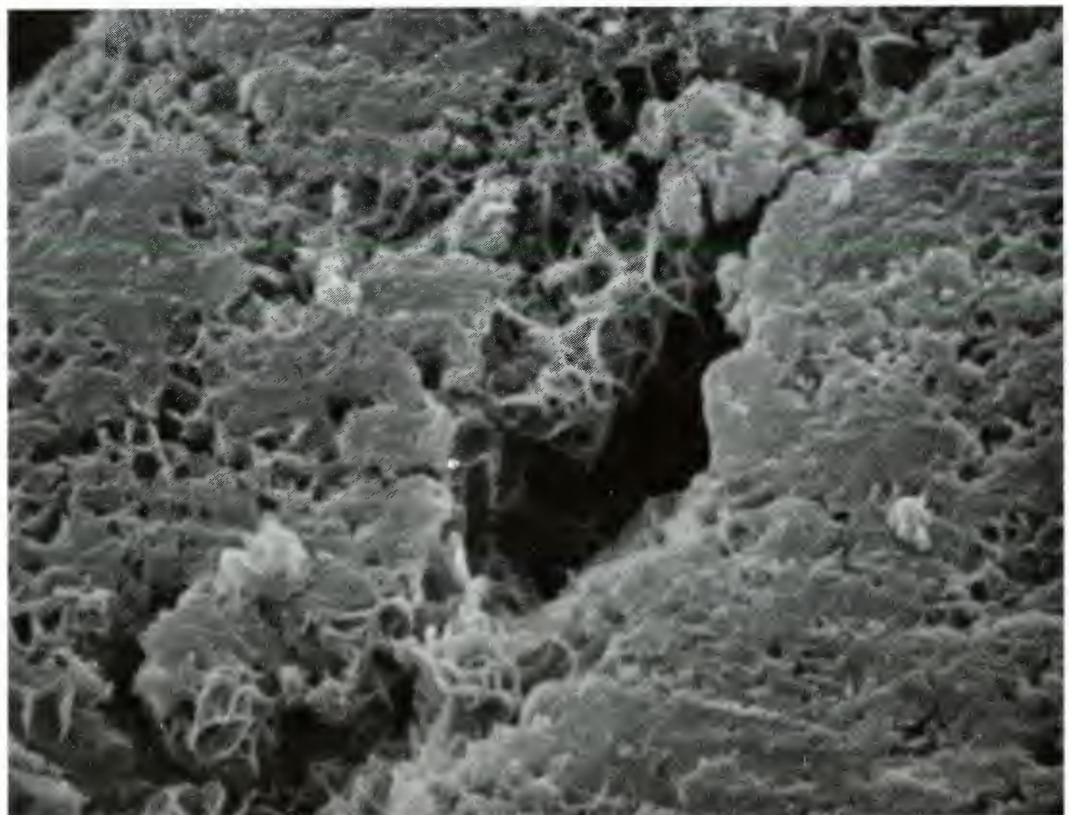

Figure 3. Enlargement of Center Area of Figure 2. Deep Pits Can Be Observed. Mangrove Forest Exposure, 5000x.

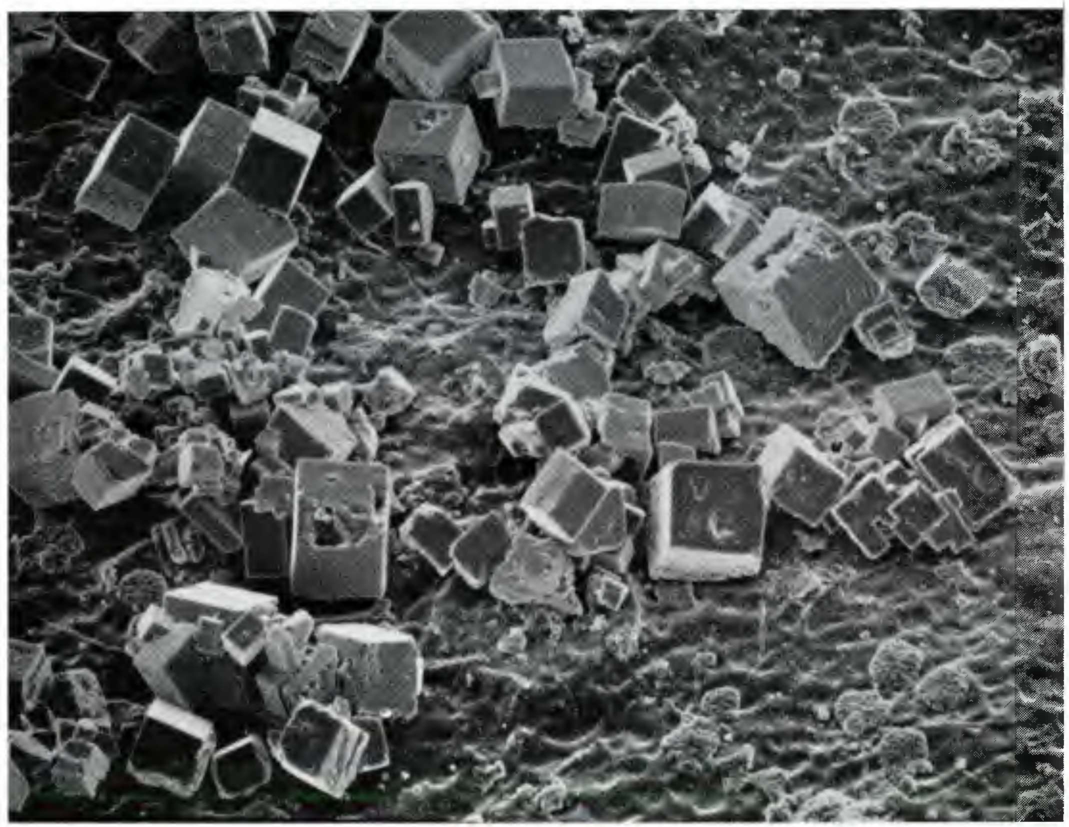

Figure 4. Sodium Chloride Crystals Found on Mangrove Leaves, 200x.

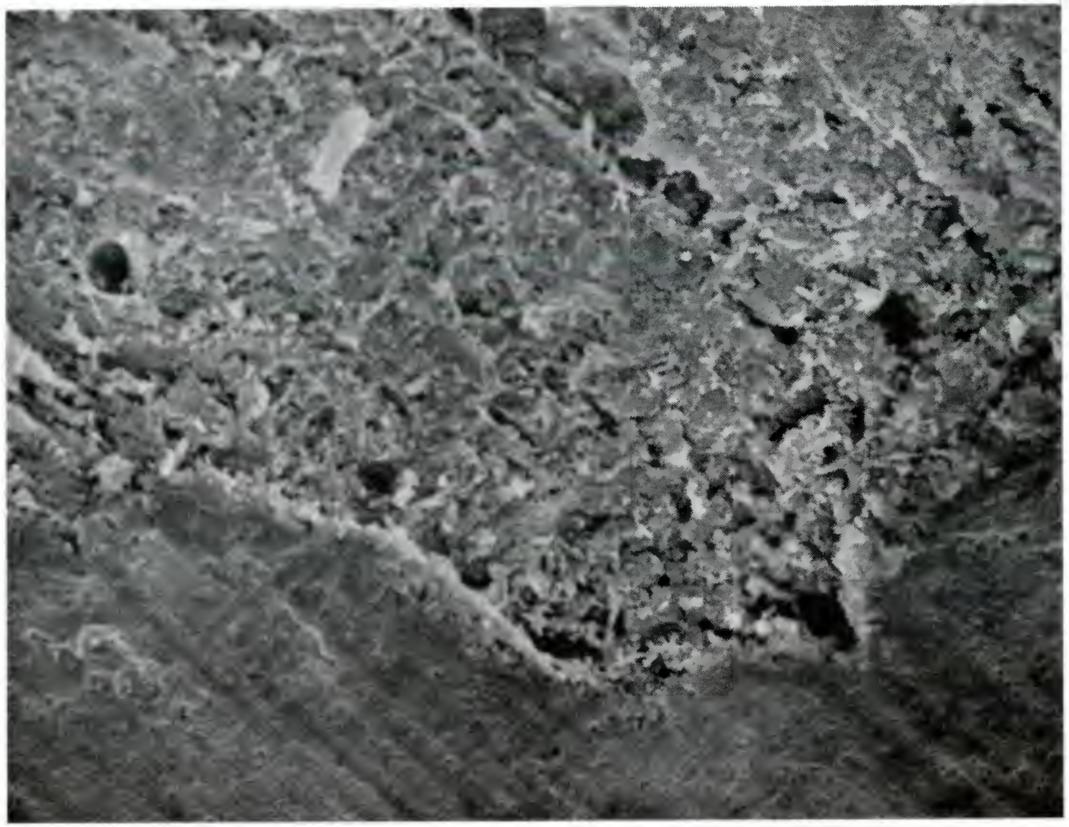

Figure 5. Borderline Between Attacked and Non-Attacked Surfaces Is Well Defined. Tannic Acid Solution Immersion Test, 2000x.

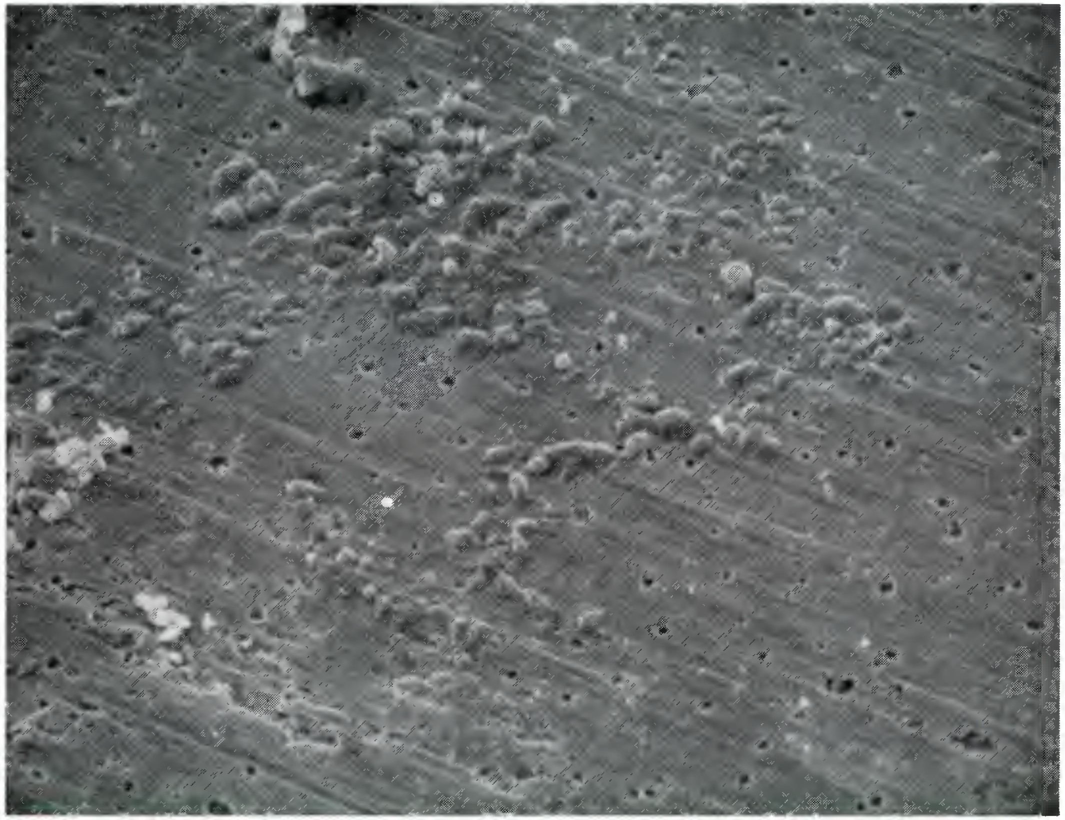

Figure 6. An Initial Development During Chloride Solution Attack Is the Formation of Pinholes. Sodium Chloride Solution Immersion Test, 1000x.

Figure 7. Pinholes, Delamination, and Formation of Rust Particles Are Observed on Surfaces. Sodium Chloride and Tannic Acid Solution Drip Test, 1000x.

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